

magnetically. The  $pK$  values were determined graphically, and the accuracy is estimated to be  $\pm 0.05$   $pK$  unit.

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## Stereochemistry of Acetolysis of Alkyl Sulfonates<sup>1</sup>

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*Acetolysis of 2-octyl *p*-toluenesulfonate at 75° for varying lengths of time gives predominantly inverted 2-octyl acetate with varying amounts of racemization. Racemization is shown to come from reaction of 2-octyl acetate with the *p*-toluenesulfonic acid also formed, from addition of acetic acid to octene formed, and from concurrent racemization of the starting tosylate. The solvolytic displacement reaction itself proceeds with essentially complete inversion of configuration. Similarly, acetolysis of benzyl- $\alpha$ -*d* tosylate gives about 20% apparent racemization in the product; this apparent racemization probably also results from concurrent racemization of the starting tosylate.*

Despite the continued widespread interest in solvolytic displacement reactions, comparatively few studies have been reported of the stereochemistry of simple alkyl systems<sup>3</sup> and even these have often lacked necessary control experiments. If we consider solvolysis in acetic acid of simple systems (not involving neighboring group participation or nonclassical carbonium ions) we find the following stereochemical outcomes:  $\alpha$ -phenylethyl chloride, 15% net inversion<sup>5</sup>;  $\alpha$ -phenylethyl tosylate, 12% net inversion<sup>6</sup>;  $\alpha$ -phenylneopentyl tosylate, 10% net inversion<sup>7</sup>; 1-butyl *p*-nitrobenzenesulfonate, 85% net inversion<sup>8</sup>; and 2-butyl and 2-octyl tosylates, varying degrees of racemization.<sup>9,10</sup> In addition, there are examples of complete inversion in systems whose stereochemistry is followed by *cis-trans*

isomerism, e.g., 4-*t*-butylcyclohexyl tosylate<sup>11</sup> and 2-indanyl-1-*d* tosylate.<sup>12</sup>

Since it is known that many acetates racemize by treatment with strong acids in acetic acid,<sup>10</sup> equivalent alkali acetate is often used during acetolysis to neutralize the sulfonic acid liberated; however, in preliminary studies of the stereochemistry of acetolysis of 2-octyl tosylate we found indications of more highly racemized product when lithium acetate was present.<sup>13</sup> Accordingly, we carried out a more extensive study.

### Results and Discussion

2-Octyl *p*-toluenesulfonate (2-OcOTs) was prepared in the usual way from optically active 2-octanol (2-OcOH) and tosyl chloride (TsCl) in pyridine. The oily product cannot be purified readily, and this product did contain some chloride, but alcohol was shown to be absent. Three separate preparations gave consistent results in the ratio of rotation of 2-OcOTs to that of 2-OcOH,  $0.98 \pm 0.01$ , a value considerably higher than the 0.84 reported by Phillips.<sup>14</sup> The relative rotations of 2-octyl acetate (2-OcOAc) and ethyl ether (2-OcOEt) to that of 2-OcOH,  $0.71 \pm 0.01$  and  $1.81 \pm 0.01$ , respectively, were determined by tetraethylammonium acetate displacement and ethanolysis, respectively, of the 2-OcOTs; these results agree with those reported earlier.<sup>15</sup>

Solvolysis of 2-OcOTs was carried out in acetic acid under various conditions, as reported in Table I. The product acetate was distilled material which was examined for purity by g.c. The observed optical activity was corrected for the presence of nonester impurities (e.g., solvent) which were considered to be racemic. The tabulated per cent net inversion is *not* corrected for the presence of several per cent of isomeric octyl acetates, mostly 3- with some 4-, whose total quantities are listed as "per cent rearrangement."

In run 73, the octyl acetate obtained shows 6% apparent racemization. This product contains 1.5% rearranged acetates, but these account for only a portion

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(2) (a) Woodrow Wilson Fellow, 1958-1960; United States Rubber Company Fellow, 1960-1961; (b) Monsanto Chemical Co. Fellow, 1956-1957.

(3) See summaries in A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1963; C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Company, New York, N. Y., 1963, Chapter 3; E. R. Thornton, "Solvolysis Mechanisms," Ronald Press Co., New York, N. Y., 1964. See also ref. 4.

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(8) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957).

(9) J. Kenyon, H. Phillips, and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(10) M. P. Balfe, W. H. F. Jackman, and J. Kenyon, *ibid.*, 965 (1954).

(11) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(12) A. Streitwieser, Jr., M. R. S. Wier, H. R. Ward, and S. S. Labana, unpublished results.

(13) These preliminary experiments were carried out by Mr. A. C. Waiss, Jr.

(14) H. Phillips, *J. Chem. Soc.*, 127, 2552 (1925).

(15) A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.* **27**, 290 (1962).

**Table I.** Acetolysis of 0.2 M 2-Octyl *p*-Toluenesulfonate at 75°

Run no.	Time, hr.	No. of half-lives <sup>a</sup>	Apparent net inversion of product, % <sup>b</sup>	Rearrangement in product, % <sup>c</sup>
49 <sup>d</sup>	26.5	~6	88.4	4.3
61 <sup>d,h</sup>	28	~6	93.2	4.6
65	260	75	39.9	18.4
73	4.75	1.4	93.5 <sup>e</sup>	1.5
154	8.7	2.5	87.8 <sup>f</sup>	4.0
54 <sup>g</sup>	26	7-8	77.9	2.1

<sup>a</sup> At 75°, the half-life is 3.5 hr. <sup>b</sup> Corrected for nonester impurities but not for rearranged esters. <sup>c</sup> Estimated error is about 5% of the number given. <sup>d</sup> The thermostat gave trouble in these runs. After the first 8-10 hr. the bath temperature dropped for a few hours. The estimate of the number of half-lives is approximate. <sup>e</sup> Ethanolsis of recovered starting material gave 2-OcOEt containing 0.9% of rearranged ether and having 92.5% of the optical activity of ether obtained from ethanolsis of the original tosylate. <sup>f</sup> Purification of the product mixture by preparative g.c. gave a product containing 99.1% 2-OcOAc corresponding to 93.3% inversion. <sup>g</sup> 0.2 M in lithium acetate. <sup>h</sup> 0.02 M 2-OcOTs.

of the apparent racemization. In run 154, the 2-OcOAc was purified by g.c. A sample of 99.1% purity had a rotation corresponding to 93% net inversion, although the solvolysis product containing 4% of rearranged acetates showed 88% apparent net inversion.

In these experiments, *p*-toluenesulfonic acid (TsOH) is liberated. Comparison of run 49 which was taken to about 98% completion with run 65 which ran for ~75 half-lives shows an increase in apparent racemization from 12 to 60%, undoubtedly because of the racemizing action of the strong acid on the secondary acetate.<sup>10</sup> However, this effect amounts to only ~1% per half-life and accounts for only a portion of the racemized 2-OcOAc produced during the first 1-3 half-lives. Furthermore, the product in run 54 which contained lithium acetate to neutralize the sulfonic acid shows *more* racemization than comparable runs without the base.

We next explore the possibility that racemic octyl acetate is produced by addition of acetic acid to octenes which may also result from solvolysis. Our solvolysis products were not examined for octenes since they were obscured by solvent in the work-up procedure used. The role of octenes as intermediates was determined by solvolysis of 2-OcOTs in acetic acid-*t*. The acetolysis products were examined for tritium with a gas-chromatograph, proportional-flow counter<sup>16</sup> with which the relative specific radioactivities could be determined for both the 2- and 3-OcOAc produced. The activity of 4-OcOAc was swamped by a tiny but highly radioactive impurity which is probably a trace of tertiary acetate. Comparison of the specific radioactivities with that of the acetic acid-*t* showed that the 2- and 3-OcOAc formed had incorporated 0.4 and 4.7-5.0%, respectively, of 1 equiv. of tritium. The isotope effect involved in the acetolysis of octene was established by reaction of an octene mixture with acetic acid-*t* containing TsOH. The octyl acetates produced showed a lower specific activity than the solvent used that corresponded to  $k_H/k_T = 12 \pm 2$ . This isotope effect corre-

sponds<sup>17</sup> to  $k_H/k_D = 5.6 \pm 0.6$ , a reasonable value for such a primary solvent isotope effect.<sup>18</sup> Application of this isotope effect to the results of 2-OcOTs solvolysis in acetic acid-*t* indicates that no more than 4% of the 2- and ~60% of the 3-OcOAc formed result from addition of solvent to octenes also formed during the solvolysis. Consequently, racemization of 2-OcOAc after formation and production of this ester from olefin account for some but not all of the racemic 2-OcOAc observed.

In run 73 the unreacted octyl tosylate was recovered. Since it could not be separated completely from octyl acetate without jeopardizing its optical purity—attempted crystallization carries the danger of optical fractionation—the material was solvolyzed in absolute ethanol. This solvolysis is known to involve complete inversion of configuration and no rearrangement; hence, the octyl ethyl ether produced is a measure of the tosylate used. The ether obtained in this way from run 73 showed 7.5% racemization and 0.9% rearrangement; that is, the unreacted tosylate recovered after 1.4 half-lives is more highly racemized than the product acetate. Moreover, the extent of this racemization leaves no significant amount of racemized acetolysis product unaccounted for. The racemized 2-OcOAc produced by acetolysis of 2-OcOTs results entirely from racemization subsequent to solvolysis, from acetolysis of olefin intermediates, and from racemization of the tosylate used concomitant with solvolysis. The acetolysis reaction itself produces 2-OcOAc with essentially complete inversion of configuration.

The racemization of the secondary alkyl sulfonate is a novel result which is most probably associated with reaction between alkyl sulfonate and the product sulfonic acid. Support for this thought comes from run 61 in which a tenfold dilution was used; the product octyl acetate is substantially less racemized. Additional support comes from experiments with added lithium tosylate discussed in the following paper.<sup>19</sup> It is shown therein that 2-OcOTs is racemized by reaction with lithium tosylate. This result also accounts for the behavior with lithium acetate in run 54; lithium acetate is converted progressively to lithium tosylate during the solvolysis.

Some years ago we reported that acetolysis of 1-butyl-1-*d* *p*-nitrobenzenesulfonate gives 1-butyl-1-*d* acetate with 85% net inversion of configuration.<sup>8</sup> In that work the acetate was shown to be optically stable for the period of a solvolysis run, *but unreacted sulfonate ester was not examined*. We thought such a control experiment was unnecessary a decade ago, but it is clearly apparent that this assumption was wrong. Similarly, optically active benzyl- $\alpha$ -*d* alcohol<sup>20</sup> was converted to the tosylate<sup>21</sup> and solvolyzed in acetic acid at 25° for about 6 half-lives. The rotation of the resulting benzyl- $\alpha$ -*d* acetate showed about 80% apparent net inversion. A control experiment showed that the ester was optically stable to the solvolysis conditions, but no such control was run with the tosylate. Analogy with the 2-octyl

(17) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *ibid.*, **80**, 5885 (1958).

(18) For example, values for  $k_H/k_D$  for the acid-catalyzed isomerization of substituted *cis*-stilbenes range from 2.4 to 6.0: D. S. Noyce, D. R. Hartter, and F. B. Miles, *ibid.*, **86**, 3583 (1964).

(19) A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, **87**, 3686 (1965).

(20) A. Streitwieser, Jr., and J. R. Wolfe, Jr., *ibid.*, **79**, 903 (1957).

(21) A. Streitwieser, Jr. and J. R. Wolfe, Jr., *ibid.*, **81**, 4912 (1959).

(16) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

case especially with the results of added salts described in the following paper<sup>19</sup> suggests that the 15–20% apparent racemization in the acetolyses of these primary systems actually results from concomitant racemization of the starting sulfonates and that complete inversion of configuration is the rule in normal acetolysis of simple primary and secondary alkyl sulfonates. The racemization observed in the secondary benzylic cases cited in the introduction appears to be too large to be accounted for in this manner; partial racemization is apparently the rule in acetolyses in which intermediate cations are involved having the stability characteristic of tertiary carbonium ions.

## Experimental

All melting points and boiling points are uncorrected. Optical rotations were taken with a Rudolph precision polarimeter on the pure liquid in 1-dm., center-fill tubes unless otherwise specified. Gas chromatographic analyses were made with an Aerograph Model A-90-C instrument (Wilkins Instrument Corp., Walnut Creek, Calif.) using 5–10 ft.  $\times$  0.25 in. columns of silicone (GE SF 96), butanediol succinate (Craig), or phenyl diethanolamine succinate (PDEAS) on firebrick.

**Acetolysis of Optically Active Benzyl- $\alpha$ -*d* Tosylate.** A solution of 11 g. (0.042 mole) of benzyl- $\alpha$ -*d* tosylate prepared<sup>21</sup> from benzyl- $\alpha$ -*d* alcohol having  $\alpha^{25D} -0.983 \pm 0.004^\circ$ ,  $\alpha^{25}_{5463} -1.216 \pm 0.013^\circ$  ( $l = 4$ ) in 250 ml. of dry acetic acid containing 2% of acetic anhydride was maintained at 25° for 21.8 days ( $\sim 6$  half-lives). The solution was diluted with cold water and extracted several times with ether. The combined extracts were washed with dilute base and water, dried with anhydrous sodium carbonate, and distilled to give 5 ml. (79%) of benzyl- $\alpha$ -*d* acetate, b.p. 99–100° (15–16 mm.), having  $\alpha^{27D} 0.230 \pm 0.005^\circ$ ,  $\alpha^{25}_{5463} 0.254 \pm 0.014^\circ$  ( $l = 4$ ). The acetate was reduced with lithium aluminum hydride in ether to give 2.4 ml. of benzyl- $\alpha$ -*d* alcohol, b.p. 94–95° (10–12 mm.), having  $\alpha^{28D} 0.309 \pm 0.005^\circ$  ( $l = 1.5$ ). Redistillation gave product having an infrared spectrum identical with that of authentic benzyl- $\alpha$ -*d* alcohol and  $\alpha^{25D} 0.304 \pm 0.004^\circ$ ;  $\alpha^{25}_{5463} 0.355 \pm 0.014^\circ$  ( $l = 1.5$ ),  $n^{25D} 1.5341$ . Compared with the alcohol used to prepare the tosylate this product shows  $82.5 \pm 1.1\%$  and  $78 \pm 3\%$  net inversion at the sodium D- and mercury 5463-lines, respectively.

**Stability of Optically Active Benzyl- $\alpha$ -*d* Acetate to Toluenesulfonic Acid–Acetic Acid.** Benzyl- $\alpha$ -*d* acetate having  $\alpha^{29D} -0.107 \pm 0.004^\circ$  ( $l = 2$ ) was prepared from benzyl- $\alpha$ -*d* alcohol having  $\alpha^{25D} -0.860 \pm 0.004^\circ$ ,  $\alpha^{25}_{5463} -1.044 \pm 0.007^\circ$  ( $l = 4$ ), by treatment with pyridine and acetyl chloride. In order to test the optical stability of benzyl- $\alpha$ -*d* acetate to the solvolysis conditions, 5 ml. was maintained for 21.8 days at 25° in solution with 250 ml. of dry acetic acid, 9.5 g. (0.05 mole) of *p*-toluenesulfonic acid monohydrate, and 10 ml. of acetic anhydride. The mixture was worked up in the same way as the solvolysis reaction to give 3.7 ml. of benzyl- $\alpha$ -*d* acetate, b.p. 98–101° (14 mm.),  $\alpha^{25D} -0.108 \pm 0.005^\circ$ ,  $\alpha^{25}_{5463} -0.148 \pm 0.008^\circ$  ( $l = 2$ ). Reduction with lithium aluminum hydride in ether gave benzyl- $\alpha$ -*d* alcohol, b.p. 97–97.5° (14 mm.),  $\alpha^{25D} -0.317 \pm 0.006^\circ$ ,  $\alpha^{25}_{5463} -0.379 \pm 0.011^\circ$  ( $l = 1.5$ ),  $n^{25D} 1.5350$ . The benzyl- $\alpha$ -*d* alcohol was recovered with  $98.3 \pm 1.9\%$

and  $97 \pm 3\%$  retention of optical activity using the sodium D- and mercury 5463-lines, respectively.

**2-Octyl *p*-Toluenesulfonate.** To a stirred solution of *p*-toluenesulfonyl chloride (1.5 moles, Eastman, filtered in benzene solution through alumina and recrystallized from hexane) in 1.5 l. of pyridine immersed in an ice-salt bath was added 90.8 g. (0.70 mole, resolved by the method of Kenyon<sup>22</sup>) of 2-octanol,  $\alpha^{28,6D} 1.915 \pm 0.003^\circ$ , over 5 hr. After storage in a refrigerator for 2 days, the mixture was poured onto ice and 1 *M* sulfuric acid and extracted with methylene chloride. After washing and drying, the solvent was replaced by hexane and treated with Darco decolorizing carbon. Hexane was removed at 1 mm. for 20 hr. at room temperature leaving 158.6 g. (80%) of colorless oil,  $\alpha^{27,7D} 1.852 \pm 0.020^\circ$ . Analysis showed 0.57% chlorine, indicating contamination by octyl chloride, but alcohol was shown not to be present by the absence of hydroxyl absorption at 2.7–2.9  $\mu$  under conditions for which a 1% solution of 2-octanol in 2-octyl tosylate showed 40% absorption at 2.8  $\mu$ .

**3- and 4-Octyl Acetates.** The alcohols were prepared by standard Grignard syntheses using the appropriate aldehydes and bromides; 3-octanol, b.p. 74–76° (10 mm.), and 4-octanol, b.p. 75–78° (10 mm.). The alcohols were converted to acetates with acetyl chloride in pyridine and ether; 3-octyl acetate, b.p. 74–76° (10 mm.), and 4-octyl acetate, b.p. 78–80° (10 mm.). Purity was monitored by g.c. analyses. Relative retention times on silicone are 2-, 1.08; 3-, 1.00; and 4-, 0.95.

**Octenes.** 2-Octanol was treated with phosphoric acid by the method of Corson and Ipatieff.<sup>23</sup> The product was filtered through alumina and distilled, b.p. 123–124°. Three olefins were detectable by g.c., and are probably 1-octene and *cis*- and *trans*-2-octene.

**Acetolyses of 2-Octyl *p*-Toluenesulfonate.** A weighed amount of dry acetic acid was preheated at  $75 \pm 0.1^\circ$  for 30 min. 2-Octyl tosylate was added from a syringe. After the desired time, the reaction mixture was poured into ice water and extracted with pentane. The extract was washed with aqueous sodium bicarbonate, dried, and distilled. The rotation was taken and corrected by the results of g.c. analysis; rearranged esters and nonester impurities were treated as being racemic. Passing optically active 2-octyl acetate through a silicone g.c. column did not change its optical activity.

When unreacted octyl tosylate was recovered, the pentane was removed under vacuum from the extract. High-vacuum (1  $\mu$ ), bulb-to-bulb distillation at room temperature afforded a colorless distillate which was redistilled to yield octyl acetate. The residue, consisting chiefly of recovered tosylate, was dissolved in 100 ml. of absolute ethanol and refluxed for 24 hr. Aqueous sodium hydroxide was added and the mixture was refluxed for several hours. The final work-up included separation of the ether–alcohol mixture by chromatography on activity I alumina before distillation of the ether. A control experiment with toluenesulfonic acid and 2-octyl acetate showed only trace conversion to octyl ethyl ether by this procedure. The rotations

(22) "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

(23) "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 152.

of acetates, ethers, and alcohols were referred to 25.0° using the data of Kenyon, *et al.*<sup>24</sup>

In a kinetic run a 0.206 *M* solution of 2-octyl tosylate in acetic acid was maintained at 75.0 ± 0.1° and titrated potentiometrically with sodium acetate in acetic acid using a Beckman Model G pH meter with calomel and glass electrodes. The integrated, first-order rate constant rose steadily with time; hence, the data in Table II were treated as in ref. 19 to give  $k_1 = 5.44 \times 10^{-5} \text{ sec.}^{-1}$ ;  $b = 1.6 \text{ l. mole}^{-1}$ . The observed time for the first half-life was 208 min.

**Table II.** Acetolysis of 0.206 *M* 2-OcOTs

Time, sec.	0	5400	12000	16800
Titer	1.06 <sup>a</sup>	10.94 <sup>a</sup>	20.30 <sup>a</sup> , 3.05 <sup>b</sup>	3.79 <sup>b</sup>
Time, sec.	25200	34200	∞	
Titer	4.66 <sup>b</sup>	5.14 <sup>b</sup>	5.78 <sup>b</sup>	

<sup>a</sup> A 10-ml. aliquot with 0.0534 *M* NaOAc. <sup>b</sup> A 5-ml. aliquot with 0.1781 *M* NaOAc.

#### *Displacement and Ethanolysis of 2-Octyl Tosylate.*

A solution of 23 g. of tetraethylammonium acetate and 23 g. of 2-octyl tosylate,  $\alpha^{29.6D} 1.512 \pm 0.003^\circ$ , in 200 ml. of acetone was refluxed for 42 hr. Vacuum distillation gave a sample of 2-octyl acetate, b.p. 45° (1.4 mm.),  $\alpha^{24.2D} -1.085 \pm 0.005^\circ$ , 99.1% pure by g.c. The impurity is solvent.

A solution of 10.03 g. of the above tosylate in 177.3 g. of absolute ethanol was refluxed for 51 hr. Distillation gave 2-octyl ethyl ether, b.p. 76° (18 mm.),  $\alpha^{26.7D} -2.739 \pm 0.002$ , of 99.2% purity by g.c. Redistillation gave material of 99.3% purity,  $\alpha^{26.7D} -2.726 \pm 0.002^\circ$ .

The ratio of rotations of 2-octyl ethyl ether and 2-octyl acetate established by these experiments, 2.51, agrees with the results of Streitwieser and Waiss,<sup>15</sup> 2.53.

*2-Octyl Tosylate in Acetic Acid-t.*<sup>25</sup> To 55.13 g. (0.918 mole) of acetic acid and 4.237 g. (0.0415 mole) of acetic anhydride containing a trace of *p*-toluenesulfonic acid was added 0.75 ml. (0.0415 mole) of water enriched with tritium to give acetic acid-*t* having  $2.90 \times 10^{10}$  d.p.m./ml. The amount of tritium in the  $\alpha$ -position was determined by treating a sample with excess ethanolic potassium hydroxide. The solution was evaporated

(24) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 99, 45 (1911); J. Kenyon and R. A. McNicol, *ibid.*, 123, 13 (1923).

(25) These experiments were carried out in the Donner Radiation Laboratory of the University of California. The authors are indebted to Mr. Fritz Woeller of the bio-organic section for his generous assistance.

and treated repeatedly with fresh ethanol and evaporated. The residue had radioactivity corresponding to  $1.91 \times 10^5$  d.p.m./ml. of the acetic acid used or  $6.6 \times 10^{-6}$  of the original activity.

A solution of 0.64 g. of 2-octyl tosylate in 10.0 ml. of acetic acid-*t* was maintained at 75° for 3 half-lives. The tube was cooled to -78° and worked up as above. The pentane solution was examined directly in a gas-chromatograph, proportional-flow counter<sup>26</sup> and the specific radioactivity was determined as counts per unit area (c.p.A.). In two such determinations, the 2-octyl acetate peak showed c.p.A. = 185 and 186; 3-octyl acetate gave c.p.A. = 2446 and 2562; compound X gave  $1.30 \times 10^5$  and  $1.18 \times 10^5$ . By comparisons between the acetic acid-*t* and toluene-*t* in liquid scintillation counting and a known mixture of toluene and 2-octyl acetate, the tritium content of the starting acetic acid-*t* corresponds to  $5.16 \times 10^4$  counts per unit g.c. area of 2-octyl acetate. Using this factor we derive the following activities relative to the acetic acid-*t* used: 2-octyl acetate, 0.004; 3-octyl acetate, 0.047–0.050; and X, 2.52–2.29. The amount of 3-OcOAc present was 3.8% of the 2-OcOAc.

Compound X was observed in very small amount; its retention time was close to 4-octyl acetate but was not identical with it; however, its high radioactivity obscured that of the 4-octyl acetate present.

*Addition of Acetic Acid-t to Octenes.* To 0.192 g. (0.0010 mole) of *p*-toluenesulfonic acid monohydrate and 0.26 g. (0.0023 mole) of octenes was added 10.0 ml. of acetic acid-*t*. After 22 hr. at 75° the dark solution was worked up as usual with a final distillation of product using toluene as a carrier. Analysis of two samples with the g.c. counter gave for c.p.A.: olefin, 988 and 786; 2-octyl acetate, 5079 and 3569; 3-octyl acetate, 5767 and 4927; and 4-octyl acetate, 10434 and 16064. The average of the 2- and 3-acetates, 4836, compared with the activity of the acetic acid-*t* used gives  $k_H/k_T = 11 \pm 2$ . To the extent that further equilibration occurs between the esters and acetic acid, this isotope effect is a minimum. The radioactivity of the recovered octenes shows that such equilibration occurs but that the effect on the isotope effect will be to increase it by about 10%. The net  $k_H/k_T$  is thus  $12 \pm 2$ .

When this isotope effect is applied to the proceeding acetolysis, we derive that (0.004)(12) or 5% of the 2-octyl acetate and (0.50)(12) or 60% of the 3-octyl acetate produced by acetolysis of 2-octyl tosylate results from acetolysis of olefin intermediate.

(26) See ref. 16. A complete description is given in T. D. Walsh, Ph.D. Dissertation, University of California, 1961.